

1 Background of The Invention:

Recent concerns regarding the environmental degradation (predominantly low level ozone formation), and the health and fire hazards associated with exposure to ammonia, volatile amines and volatile organics (VOCs), has led to increasingly strict regulatory limitations on the nature, and proportions, of VOCs which may be employed in coatings. One technique that has been employed in order to comply with said limitations in latex coating applications is the development of self coalescing latex resins which require no coalescents. However, to date, such materials have had the disadvantage of being limited to low Tg film formers with poor performance properties.

25 This invention teaches the use of low levels of combinations
26 of nonvolatile reactive amines, in combination with hydroxyl

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1 bearing unsaturated esters and/or ethers and/or ether-esters,
2 and/or non-hydroxyl bearing unsaturated esters and/or ethers
3 and/or ether-esters and incompletely etherified and/or esterified
4 oligomeric glycols and/or oligools as partial or full replacements
5 for conventionally employed volatile amines and/or ammonia as
6 neutralizers, and organic solvents as coalescents, respectively,
7 in latex resin applications. This invention has the advantage of
8 reducing emissions and enhancing the performance of films produced
9 from conventional latex resins, and when employed in conjunction
10 with certain types of hypersurfactants (cf. Table 5) also
11 upgrades pigment and/or extender dispersion, and reduces grind
12 times in particulate containing variants; thus enhancing plant and
13 energy use efficiencies. Synergistic performance enhancement, and
14 VOC reduction in latex resins may be attained via the employment
15 of the aforementioned technologies in combination. Partial
16 replacement of either or of both of the aforementioned components
17 by the alternatives of this invention is shown to provide lesser,
18 but still desirable benefits.

19 Preferred Embodiment of The Invention

20 The non-volatile reactive amines useful in the practice of
21 this invention have vapor pressures below 0.1 mm Hg at 25°C,
22 contain at least one basic nitrogen, and at least one carbon to
23 carbon double bond, and/or a transition metal ligand, and contain
24 no more than twelve carbon atoms per basic nitrogen atom. Those
25 more preferable contain one or more (meth)acryl and/or N-vinyl
26 ligands, and those most preferable have a water solubility

1 exceeding 2% at 25°C. Specific examples of such useful non-
2 volatile reactive amines are given in Table (1). These examples
3 are intended to be illustrative rather than exhaustive of the
4 scope of useful materials.

6 TABLE I

| | | |
|----|------|--|
| 7 | (1A) | N-vinyl pyrrolidone |
| 8 | (1B) | N,N,N'-tris (2-butenyl), ethylene diamine |
| 9 | (1C) | N', methyl-1, 3-propylene diamine mono 2- propenamide |
| 10 | (1D) | N, 2-propenyl, bis (2-hydroxy)propyl amine |
| 11 | (1E) | N, 2-propenyl, N'- (2-hydroxy)ethyl, hexamethylene |
| 12 | | triamine |
| 13 | (1F) | 4-(N, 3-hydroxypropyl, N-vinyl) 2-amino ethyl 2-butenolate |
| 14 | (1G) | 2-[N, -(2-oxa-cyclopentadienyl)] amino acetic acid ethyl |
| 15 | | ester |
| 16 | (1H) | 4-(N,N bis vinyl) 1,3-pentanediol |
| 17 | (1I) | tetraethylene glycol mono 3-(N, ethyl) amino, 2-(methyl) |
| 18 | | 2-propenoate |
| 19 | (1J) | N,N-divinyl glutamic acid 2-propenyl ester |
| 20 | (1K) | 6-(N,N bis vinyl) hexanoic acid ethyl ester |
| 21 | (1L) | Titanium IV tetrakis N, 2-aminoethyl ethanolato |

22 The preferred types of the hydroxyl bearing, unsaturated
23 esters and/or ethers and/or ether-esters useful in the practice
24 of this invention are those having vapor pressures below 0.1 mm
25 Hg at 25°C, which are capable of air initiated, oxidative
26 oligomerization and/or polymerization derived non-reversible

1 bonding, under normal latex application conditions, to film
2 component(s) and/or to substrate, in order to maximize coating
3 properties via crosslinking the resulting latex thereby
4 minimizing its (post film formation) environmental sensitivity.
5 Examples of such unsaturated esters and ether and ether-esters as
6 are useful in the practice of the instant invention are provided
7 in Table II. These examples are intended to be illustrative
8 rather than exhaustive of the scope of useful materials.

9 Table II

- 10 (2A) trimethylol propane bis (2-methyl)-2-propenoate ester
11 (2B) sorbitan tetrakis 2-butenate ester
12 (2C) bis pentaerythritol 2-propenolate, tris 2-propenoate ester
13 (2D) hexanoic acid 6-hydroxy, (2-propenoate)ethyl ester
14 (2E) citric acid mono isodecenyl ester
15 (2F) malic acid bis cinnamyl ester
16 (2G) 3-heptanoyl furfuryl alcohol
17 (2H) 1,2,3-propanetriol 1-vinyl ether, 2-phenyl carboxylate ester
18 (2J) trimeric 2-butenediol mono (methyl) glutarate ester
19 (2K) ethoxylated (4) bis phenol A mono 2-propenoate ester

20 The preferred types of the non-hydroxyl bearing unsaturated
21 esters and/or ethers and/or ether-esters useful in conjunction with
22 the practice of this invention are those having vapor pressures
23 below 0.1 mm Hg at 25°C, which are capable of air initiated
24 oxidative oligomerization and/or polymerization, and non-reversible
25 bonding, under normal latex application conditions, to film
26 component(s) and/or to substrate, in order to maximize coating

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properties via crosslinking the resulting latex thereby minimizing its (post film formation) environmental sensitivity. Examples of such non- hydroxyl bearing unsaturated esters and ether and ether-esters as are useful in the practice of the instant invention are provided in Table III. These examples are intended to be illustrative rather than exhaustive of the scope of useful materials.

Table III

- (3A) trimethylol propane bis (2-methyl)-2-propenoate ester, mono vinyl ether
- (3B) 1,2,3-propane triol tris 2-butenate ester
- (3C) penta erythritol 2-propenolato, tris 2-propenoate ester
- (3D) hexanoic acid 6-acetoxy, (2-propenoato)ethyl ester
- (3E) fumaric acid bis isodecyl ester
- (3F) maleic acid bis cinnamyl ester
- (3G) furoic acid vinyl ester
- (3H) 1,2,3-hexanetriol 1,2-bis vinyl ether, phenyl carboxylate ester
- (3J) trimeric 2-butene-1,4-diol bis propionate ester
- (3K) ethoxylated (4) bisphenol A bis 2-(methyl)-2-propenoate ester

The preferred types of the incompletely etherified and/or esterified oligomeric glycols and/or oligools useful in the practice of this invention are those having vapor pressures below 0.1 mm Hg at 25°C, which are oligomers of two to 4 carbon diols, and of three to six carbon triols, wherein each of the ether and/or ester ligands contains five or fewer carbon atoms per oxygen.

1 Examples of such incompletely etherified and/or esterified
2 oligomeric glycols and/or oligoals as are useful in the practice of
3 the instant invention are provided in Table IV. These examples are
4 intended to be illustrative rather than exhaustive of the scope of
5 useful materials.

6 Table IV

- 7 (4A) penta (ethylene glycol) mono methyl ether
8 (4B) tetra (1,4-butylene glycol) mono (2-methyl) butyrate
9 (4C) 1-hydroxy-2,5-bis methyl-3,6,9,12-tetraoxa tetradecane
10 (4D) 4-oxaheptane-1,2,6,7-tetraol mono acetate, mono 2-propyl
11 ether (mixed isomers)
12 (4E) ethoxylated (6) 1,2,4-butanetriol bispropanoate (mixed
13 isomers)
14 (4F) tris 1,2,5-n pentane triol tetraethyl ether (mixed isomers)
15 (4G) tris (1,3-propane-diol) mono isopentyl ether
16 (4H) 1,2- bis (2- hydroxy ethoxy ethyl) 1,2,3-propane triol
17 (4J) polyethylene glycol (300) mono amyl ether
18 (4K) tris neopentyl glycol mono n-propyl ether

19 The surfactants most useful in the practice of this invention
20 are those having vapor pressures below 0.1 mm Hg at 25°C, which are
21 capable of non-reversible bonding, under normal processing
22 conditions, to film component(s) and/or substrate in order to
23 maximize coating properties, while minimizing post film formation
24 environmental sensitivity, and which serve to efficiently wet
25 substrates coated, and to disperse particulates, if any, employed
26 in the formulated latex coating. Among the surfactants found to be

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1 useful in the practice of this invention are amphoteric detergents,
2 and certain organometalics based on tetravalent titanium or
3 zirconium. These last have been found to contribute significantly
4 to substrate adhesion and improved corrosion resistance on wood,
5 metallic and ceramic substrates, and to be particularly useful in
6 maximizing color intensities of carbon black, azo and
7 phthalocyanine based pigments. Specific examples of the preferred
8 types of hypersurfactants are given in Table V. These examples are
9 intended to be illustrative rather than exhaustive of the scope of
10 useful materials.

11 Table V

- 12 (5A) 12-N,N,N-trimethylaminododecanoato
13 (5B) N-(pentakis oxyethylene sulfato) triethylene diamine
14 (5C) p-[6-N(methyl) morpholino]octyl phenyl phosphonic acid
15 (5D) N,N,N-triethyl glutamic acid
16 (5E) titanium 4 octyl, [(tris octyl) diphosphato
17 (5F) titanium 4 oxoethylene, bis (dodecyl) phenylsulfonato
18 (5G) oxy [bis titanium 4 (bis tridecyl) diphosphate]
19 (5H) zirconium 4 tetraethylene glycol monomethyl ether, tris
20 (tetraethylene glycol monomethyl ether) diphosphato
21 (5J) zirconium 4, bis w-N,N-(dimethyl)amino octanoato, 1,4-
22 cyclohexanediolato
23 (5K) triethylene glycol diolato, bis [zirconium 4 tris (octyl)
24 phosphate]

25 Those skilled in the art shall no doubt be capable of
26 subverting the teachings of this invention via the substitution of

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1 functionally equivalent materials, e.g. employment in combination
2 of hydroxylated and non-hydroxyl bearing esters (ether-esters)
3 optionally in combination with partially esterified and/or
4 etherified glycols, and or polyols, in place of either component
5 (set) alone, (as is amply demonstrated in example No. 4.), or of
6 unsaturated analogous unsaturated amides, for a portion of the
7 aforementioned unsaturated ethers, esters or ether-esters disclosed
8 above, and/or fluorination of one or more of the species of
9 components heretofore described as necessary to the successful
10 practice of this invention; however such non-critical
11 modifications, and/or combinations of relevant species types, must
12 be considered as within the scope of this disclosure.

13 Further amplification of the scope and utility of the instant
14 invention to latex coating applications in inks, paints and stains
15 shall be found to be illustrated by the content(s) of examples 1
16 through 5. Said examples are intended to be illustrative rather
17 than exhaustive of the extraordinarily diverse applicability of the
18 instant invention.

19 Example #1

20 This example teaches the superiority of the present invention
21 versus the prior art with respect to the productivity, VOC
22 emissions, and performance quality in a masonry sealer application.

23 A masonry sealer formulation was prepared by the sequential
24 dispersion of the indicated components (pigment dispersion times
25 and grind quality achievement was noted). The resulting sealer was
26 applied via roller to smooth surface, ten day old, 8" X 18" X 1"

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thick concrete castings, at an application rate of one gallon per 400 square foot, dry time (to touch) was measured under conditions of 72° F and 85% humidity. After 240 hours of drying @ 72° F and 85% humidity, sealer performance was measured by weighing the dry casting, then impounding a 6" depth of water, or alternatively 6% salt solution, on such a casting for twenty four hours, then draining and weighing the drained casting. The weight percent of water, and independently that of 6% salt solution, adsorbed by said castings were used to determine sealer efficacy. The results of this study are given in Table No. 1.

Formulation: in parts by weight; (in order of addition) water 200.0; neutralizer¹, as shown; surfactant^a, as shown, biocides², 18.50; hydroxy ethyl cellulose, 5.00; potassium tris polyphosphate, 2.00; defoamer², 1.00; coalescent^a, as shown; ultramarine blue pigment, 0.25; rutile titanium dioxide, 200.0, American process zinc oxide, 25; platey talc, 250; water, 49.98; AC-625 Acrylic latex resin³, 352.0; defoamer², 0.98; surfactant^b, coalescent^b, as shown,; water, 24.99; and sodium nitrite 2.30; thixotrope⁴, as shown (required) to adjust system viscosity to 85-90 KU at 75° F.

Table No. 1

| <u>Formulation</u> | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> |
|--------------------|--------------------------------|----------|----------|----------|----------|
| neutralizer | amp-95/1.98 | 1B/2.00 | 1H/1.80 | 1G/2.20 | 1D/1.78 |
| surfactant(a) | Tamol 850 ⁷ /14.85 | 5A/1.80 | 5E/1.75 | 5K/1.55 | 5H/1.50 |
| coalescent(a) | Propylene glycol /34.56 | none | none | 4J/4.50 | none |
| surfactant(b) | Triton N101 ³ /2.20 | none | 5B/1.00 | none | 5D/1.25 |
| coalescent(b) | Texanol ⁸ /9.88 | 2A/16.42 | 3A/12.60 | 3F/18.55 | 2H/11.70 |

| <u>Formulation</u> | <u>6</u> | <u>7</u> | <u>8</u> | <u>9</u> | <u>10</u> |
|--------------------|--------------------------------|-------------------------|------------------------|----------|---------------------------|
| neutralizer | ammonia/1.00 1L/1.00 | 1B/1.00 ammonia/1.00 | 1H/1.80 AMP-95/1.00 | 1G/1.20 | 1D/1.78 |
| surfactant (a) | Tamol 850 ⁷ /14.85 | 5A/1.80 | 5E/0.75 | 5K/1.55 | 5H/0.75 |
| surfactant (b) | Triton N101 ⁶ /2.20 | none | Triton N101 /2.20 | none | 5D/1.25 |
| coalescent (a) | Propylene glycol /34.56 | none | none | 4J/4.50 | Propylene glyco /17.88 |
| coalescent (b) | Texanol ⁸ 19.98 | 2A/16.42 | 3A/12.60 | 3F/18.55 | 2H/5.85 |

| <u>Formulation</u> | <u>VOC g/l⁵</u> | <u>Dispersion time hr.</u> | <u>Grind Hegman</u> | <u>Water adsorption g.</u> | <u>Salt water adsorption g.</u> |
|--------------------|----------------------------|--------------------------------|-------------------------|--------------------------------|-------------------------------------|
| 1 | 124 | 3.4 | 4 | 46 | 61 |
| 2 | 8 | 0.7 | 6 | 27 | 32 |
| 3 | 3 | 0.6 | 6 | 21 | 28 |
| 4 | 5 | 0.7 | 5 | 24 | 27 |
| 5 | 4 | 0.6 | 6 | 25 | 30 |
| 6 | 112 | 3.1 | 4 | 37 | 48 |
| 7 | 10 | 0.7 | 6 | 32 | 42 |
| 8 | 3 | 2.4 | 5 | 27 | 38 |
| 9 | 6 | 0.7 | 5 | 24 | 27 |
| 10 | 36 | 1.8 | 6 | 31 | 39 |

Notes: a) As shown; 1) A combination of 3.5 parts of Nuosept 95, and 15 parts of Nuocide 404D, Huls Corp. were employed; 2) Defo 806-102; Ultra Inc. 3) AC-625, Union Carbide Corp.; 4) Rhevis CR, Rhevis Corp. 5) via EPA Method 24GC; 6) Rohm and Haas Corp.; 7) Eastman Kodak Inc.

The efficacy of the coalescent systems of the instant art in producing a less water and salt permeable, acrylic latex based masonry seal coating, is compared to a conventionally coalesced counterpart, Formulation No. 1, and is obvious from the preceding data. VOC emissions reduction and improvement in both productivity and dispersion level achieved are likewise self evident.

Example #2

This example teaches the superiority of the present invention versus the prior art with respect to the productivity, VOC

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1 emissions, and performance quality in a direct to metal,
2 maintenance coating application.

3 Direct to metal coatings were prepared by the sequential
4 dispersion of the indicated components (pigment dispersion times
5 were noted). The resulting coating was spray applied to sandblasted
6 smooth surface 24" X 8" carbon steel test panels at application
7 rate of one gallon per 250 square feet. After 120 hours of drying
8 @ 72° F and 85% humidity, edge sealing and scribing, the coatings'
9 corrosion resistance performance were each measured by QUV cabinet
10 exposure [cyclic exposure to UV radiation, 4% saline solution, and
11 varying temperature (25°-80° C)].

12 **Formulation:** in parts by weight (in order of addition): water,
13 50.0; neutralizer, as shown; Surfactant^a, as shown, biocide¹, 4.00;
14 oxidized polyethylene wax, 4.00; (disperse wax) polyurethane
15 thixotrope², as shown; defoamer³, 2.00; coalescent^a, as shown,
16 ultramarine blue pigment, 0.25; rutile titanium dioxide, 125; zinc
17 aluminate 150; Acrylic latex resin⁴, 64.0; (disperse particulates
18 to Hegman 7.5+). Neutralizer, is shown; acrylic latex resin⁴,
19 564.0; defoamer², 0.98; surfactant^b, coalescent^b, as shown; water,
20 16.00; arid sodium nitrate 2.30. Thixotrope², (as required) to
21 adjust system viscosity to 80-85 KU at 75° F . The control coating
22 required 3.7 hours to disperse to a Hegman grind gauge reading of
23 7+, whereas each of the instant art coatings achieved said fineness
24 of grind in less than one half hour. The results of this study are
25 given in **Table No. 2**

Table No. 2

| <u>Formulation</u> | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> |
|-------------------------|---------------------------------|--------------------------|-------------------|-------------------------------|-----------|-----------------------------|
| neutralizer | DMAMP-80 ⁵ /12.5 | 1A/4.00 | 1C/1.80 | 1E/2.20 | 1J/1.78 | DMAMP-80 ⁵ /6.25 |
| surfactant (a) | Triton CF10 ⁶ /10.00 | 5D/1.80 | 5F/1.75 | 5C/1.55 | 5J/1.50 | 1A/ 2.00 |
| thixotrope ² | 15.00 | 5.00 | 5.50 | 8.70 | 5.30 | Triton CF 10/5.00 |
| coalescent (a) | Diproylene glycol /34.60 | 4B/12.00 | 4E/10.5 | 4K/8.25 | none | 9.32 |
| surfactant (b) | none | none | 5A/1.00 | Triton CF10 ⁶ .4.0 | none | 5D/1.25 |
| coalescent (b) | PmPE ⁷ /44.60 | 2A/16.42 | 3A/12.60 | 3F/18.55 | 2H/14.70 | 2H/14.70 |
| thixotrope ² | 21.40 | 3.20 | 1.50 | 0.70 | 2.30 | 1.95 |
| <u>Formulation</u> | <u>7</u> | <u>8</u> | <u>9</u> | <u>10</u> | <u>11</u> | <u>12</u> |
| neutralizer | DMAMP-80 ⁵ /12.5 | 1A/4.00 | 1C/1.80 | 1E/2.20 | 1J/1.78 | DMAMP 80 ⁵ /6.25 |
| surfactant (a) | Triton CF10 ⁶ /10.00 | 5D/1.80 | 5F/1.75 | 5C/0.55 | 5J/1.50 | Triton CF10/5.00 |
| surfactant (b) | none | none | 5A/1.00 | Triton CF10 ⁶ /2.0 | none | 5D/1.25 |
| thixotrope ² | 15.00 | 5.00 | 5.50 | 8.70 | 5.30 | 9.32 |
| coalescent (a) | Dipropylene glycol /17.3 | PmPE ⁷ /22.60 | 4B/12.00 | 4E/10.5 | 4K/8.25 | PmPE ⁷ /22.3 |
| coalescent (b) | 2A/ 8.81 | 2A/ 6.42 | PmPE ⁷ | 3F/ 18.55 | 2H/14.70 | 2H/14.70 |
| thixotrope ² | 18.90 | 6.20 | 4.50 | 3.70 | 2.30 | 6.95 |

| <u>Formulation</u> | <u>VOC g/l⁸</u> | <u>Initial gloss</u> | <u>60° gloss @</u> | <u>60° gloss @</u> | <u>60° gloss @</u> |
|--------------------|----------------------------|----------------------|--------------------|---------------------|----------------------|
| | | <u>@60°</u> | <u>200hr. QUV</u> | <u>500 hr. QUV.</u> | <u>1,000 hr. QUV</u> |
| 1 | 232 | 82 | 76 | 31 | film destroyed |
| 2 | 9 | 91 | 87 | 82 | 76 |
| 3 | 11 | 93 | 90 | 88 | 80 |
| 4 | 8 | 87 | 86 | 82 | 61 |
| 5 | 10 | 88 | 86 | 85 | 84 |
| 6 | 13 | 84 | 80 | 66 | 59 |
| 7 | 72 | 85 | 79 | 46 | 12 |
| 8 | 57 | 80 | 76 | 51 | 18 |
| 9 | 28 | 87 | 84 | 72 | 63 |
| 10 | 7 | 88 | 86 | 84 | 78 |
| 11 | 8 | 92 | 90 | 87 | 85 |
| 12 | 77 | 85 | 80 | 75 | 48 |

Notes: 1) Nuosept 95, -Huls Corp. 2) Acrysol RM 2020, Rohm and Haas 3) Defo 3000; Ultra Inc. 4) HG 56, Rohm and Haas Corp. 5) 80%

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1 2-N,N-dimethylamino-2-methyl propanol aq. 6) Union Carbide Corp. 7)
2 propylene glycol mono phenyl ether. 8) via EPA Method 24GC

3 The efficacy of the coalescent systems of the instant art in
4 producing a more environmentally resistant, acrylic latex based
5 direct to metal coating, as compared to a conventionally coalesced
6 counterpart, Formulation No. 1, is obvious from the preceding data.
7 VOC emissions reduction, and improvement in productivity achieved
8 are likewise self evident.

9 Example #3

10 This example teaches the superiority of the present invention
11 versus the prior art with respect to productivity, VOC emissions,
12 and performance quality in a polyvinyl acetate based interior flat
13 architectural paint application.

14 Interior flat paints, were prepared by the sequential
15 dispersion of the indicated components (pigment dispersion times,
16 and dispersion efficacy were noted). The resulting coating was
17 brush applied to unprimed drywall (gypsum sheet) @ 72° F and 80%
18 humidity, coverage, stain removal, and scrubability performance
19 were each measured after 7 days of drying 72+/- 2° F @ 65-80%
20 humidity.

21 Formulation; in parts by weight; (in order of addition) water,
22 200.0; neutralizer¹, as shown; surfactant^a, as shown, biocides²,
23 1.00; hydroxy ethyl cellulose, as shown; potassium tris
24 polyphosphate, as shown; defoamer³, 1.00; coalescent^a, as shown;
25 ultramarine blue pigment, 0.25; rutile titanium dioxide, 250.0,
26 water washed clay⁴, 50.0; calcium carbonate⁵, as shown; diatomite⁶,

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5 The results of this evaluation are shown in Table No. 3.

| Table No. 3 | | | | | | |
|-------------------------|--|--------------------------|---------------------------|-----------------------------------|----------|------------------------------------|
| Formulation | 1 | 2 | 3 | 4 | 5 | 6 |
| neutralizer | 28% ammonia aq. 6.05 | 1B/2.00 | 1H/1.80 | 1G/2.20 | 1D/1.78 | 28% ammonia 6.05 |
| HEC(QP-4400) | 5.50 | 1.20 | 1.35 | 1.25 | 1.40 | 1.35 |
| surfactant(a) | Tamol 731/6.90 Triton N101/3.31 | 5E/1.80 | 5J/1.75 | 5C/1.55 | 5F/1.5 | Tamol 731/6 Triton N101/3.31 |
| coalescent(a) | Propylene glycol /51.95 Texanol/9.88 | 4A/6.00 | 4 F/7.00 | 4H/5.50 | 4E/7.00 | 4E/7.00 |
| Calcite | 50 | 150 | 125 | 150 | 140 | 50 |
| coalescent(b) | none | 2A/26.4 | 3C/12.60 | 3F/18.50 | 2J/11.90 | 2J/11.90 |
| thixotrope ^g | 3.5 | 3.0 | 3.1 | 2.7 | 2.4 | 3.9 |
| Formulation | 7 | 8 | 9 | 10 | | |
| neutralizer | 28% ammonia aq. 6.05 | 1B/2.00 | 1H/1.80 | 1H/1.80 | | |
| HEC (QP-4400) | 5.50 | 1.20 | 1.35 | 1.25 | | |
| surfactant(s) | Tamol 731/ 6.9 Triton N101/ 3.31 | Tamol 731/ 3.9 5J/1.0 | 5J/ 1.75 | Tamol 731/ 6.9 Triton N101/ 3. | | |
| coalescent (a) | Propylene glycol 51.95 | 4A/6.00 | Propylene glycol 51.95 | 4H/5.50 | | |
| calcite | 50 | 100 | 125 | 150 | | |
| coalescent (b) | 4E/2.00 | 2A/ 26.4 | 3C/ 12.60 | 3F/ 18.50 | | |
| thixotrope ^g | 3.5 | 3.0 | 3.1 | 2.7 | | |

| <u>Formulation</u> | <u>VOC g/l⁹</u> <u>hr.</u> | <u>Dispersion Time</u> | <u>Grind</u> <u>Hegman</u> | <u>Min.Coalescence</u> <u>temp °C</u> | <u>Scrubs¹⁰</u> | <u>Stain Removal¹¹</u> |
|--------------------|--|------------------------|-------------------------------|--|----------------------------|-----------------------------------|
| 1 | 199 | 2.4 | 4 | 47 | 410 | 6 |
| 2 | 8 | 0.4 | 5 | 34 | 1,740 | 9 |
| 3 | 3 | 0.6 | 6 | 32 | 2,025 | 10 |
| 4 | 5 | 0.6 | 6 | 36 | 1,960 | 9 |
| 5 | 4 | 0.5 | 5 | 30 | 2,230 | 10 |
| 6 | 15 | 2.2 | 4 | 31 | 785 | 8 |
| 7 | 190 | 2.4 | 4 | 43 | 850 | 7 |
| 8 | 9 | 0.9 | 5 | 35 | 1,140 | 8 |
| 9 | 188 | 1.1 | 5 | 45 | 890 | 7 |
| 10 | 8 | 2.4 | 4 | 37 | 1,310 | 8 |

Notes: 1) As shown; 2) Nuosept 95, Huls Corp.; 3) Defo 3000; Ultra Inc.. 4) 70C Huber Corp. 5) Camel Carb., Cambel Corp.; 6) Diafil 530

viscosity of 65-70 KU, and the coating was applied by curtain coating on sanded but unprimed 4' X 8' X 0.25" laminate natural oak (on pine) substrate. The coated panels were force dried by passing same through a 180° F oven for 20 minutes, then cooled at ambient temperature (ca. 80° F) for 24 hours prior to evaluation, for abrasion and solvent resistance. to determine coating performance, efficacy. The results of this study are given in Table No. 4.

Table No. 4

| Formulation | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------|------|------|------|
| <u>Part A:</u> | | | | | | | | |
| neutralizer | 28% | 1A | 1H | 1H | 1H | 1B | 1B | 1B |
| | ammonia aq. | | | | | | | |
| <u>Part B: formulation</u> | | | | | | | | |
| Texanol | 8.00 | | | | | | 4.00 | 4.00 |
| diethylene glycol | 18.20 | | | | | | 9.10 | 9.10 |
| mono butyl ether | | | | | | | | |
| 2A | | 12.05 | 6.00 | | 6.00 | 6.00 | 6.00 | |
| 2C | | | 4.40 | 10.70 | | | | |
| 3B | | | | | 4.20 | | | 6.00 |
| 4G | | | 1.90 | 2.90 | 1.05 | 6.20 | | |
| 4J | | | | | | | | |
| Formulation | VOC g/l ¹ | Abrasion | Solvent | Stain | Mix pot life | | | |
| | resistance ² | resistance ³ | resistance ⁴ | hr. @ 80°F ⁵ | | | | |
| 1 | 165 | 114 | lifts | poor | 7.5 | | | |
| 2 | 3 | 31 | slight softening | good | 42 | | | |
| 3 | 4 | 29 | slight softening | fair | 35 | | | |
| 4 | 3 | 24 | no change | excellent | 40 | | | |
| 5 | 3 | 26 | no change | good | 61 | | | |
| 6 | 4 | 98 | mod. Softening | fair | 46 | | | |
| 7 | 83 | 19 | slight softening | fair | 21 | | | |
| 8 | 85 | 78 | severe softening | poor | 11 | | | |

Notes: 1) By EPA Method 24GC; (formulations 2 through 7 produced 0 to negative VOC readings by EPA Methods 24, and 24A; 2) Tabor CS-10 wheel 1000 cycles; 3) 24 hr methyl ethyl ketone covered spot test; 4) 24 hr exposure to lipstick; 5) time to 10% loss of abrasion resistance in finished coating.

This example demonstrates, that the use of the combination of components cited as the basis of the instant invention, viz. That

1 Whittaker, Clark, and Daniels Inc. 7) Rhoplex 3077, Rohm and Haas
2 Corp.; 8) Rhevis CR, Rhevis Corp. 9) via EPA Method 24GC. 10) ASTM
3 method; 11) ASTM method.

4 The efficacy of the coalescent systems of the instant art in
5 producing a more, scrub and stain resistant PVA latex based
6 interior flat architectural coating as compared to a conventionally
7 coalesced counterpart, Formulation No. 1, is obvious from the
8 preceding data. VOC emissions reduction and improvement in both
9 productivity and dispersion level achieved are likewise self
10 evident, as is a considerable reduction in minimum coalescence
11 temperature, without recourse to the use of low boiling, flammable
12 solvent(s), normally employed to induce same.

13 Example #4

14 This example teaches the superiority of the present invention
15 versus the prior art with respect to the productivity, VOC
16 emissions, and performance quality in a force dried, clear,
17 protective, two component acrylic latex cured - waterborne epoxy,
18 wood cabinet coating.

19 Component A. neutralizing agent, as shown-3.5 PBW; sodium
20 nitrite 0.15 and defoamer (Patcote 519-Patco Coatings Inc.) were
21 admixed with 95.85 PBW of (Acrylic latex-Maincote AE 58), and said
22 emulsion was subsequently mixed with 50 PBW of Component B,
23 formulated by blending various additives, as shown, into 12.5 PBW
24 of Genepoxy 370-H55- Daubert Chemical Co., and diluting as
25 necessary with water to produce a total part B weight of 25 parts.
26 Thixatrop¹, was added, as required, to provide an initial mix

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1 nonvolatile reactive amines, in combination with hydroxyl bearing
2 unsaturated esters and/or ethers and/or ether-esters, and/or non-
3 hydroxyl bearing unsaturated esters and/or ethers and/or ether-
4 esters and incompletely etherified and/or esterified oligomeric
5 glycols and/or oligools as (partial or full) replacements for
6 conventionally employed volatile amines and/or ammonia as
7 neutralizers, and organic solvents as coalescents, respectively may
8 be employed to substantially enhance the processability (pot life),
9 mechanical and chemical resistance properties (abrasion and stain
10 resistance respectfully) as well as attain VOC reduction in wood
11 coatings. A further benefit of the instant invention as applied to
12 wood coatings is that unlike conventionally coalesced waterborne
13 coatings, e.g. formulation D-1 latex formulations based upon the
14 teachings of this invention, e.g. formulations D-2 through D-7, do
15 not cause significant grain rise, thereby virtually eliminating the
16 necessity for intercoat sanding. These data also demonstrate that
17 subsets of the preferred combination of components herein disclosed
18 (e.g. formulations D-3,D-5, and D-6) may provide considerable
19 benefits relative to their conventional counterparts, such as
20 Formulation No. 1; however, omission of one or more of the
21 components of the combination herein disclosed leads to inferior
22 results as compared to the inclusion of the full compliment.

23 Example #5

24 This example teaches the superiority of the present invention
25 versus the prior art with respect to the productivity, VOC
26 emissions, and performance quality in waterborne flexographic inks.

A latex flexographic ink formulation, was prepared by the sequential dispersion of the indicated components (pigment dispersion times and grind quality achievement was noted). The resulting ink was applied via a #6 wire wound rod to bond paper, and permitted to dry. Dry time (to touch) was measured under conditions, of 72° F and 85% humidity. After 6 hours of drying @, 72° F and 85% humidity, heat seal resistance performance (face to face) was measured at 25 psig. and 2 seconds contact time) the results of this study are given in Table No. 5.

Formulation: in parts by weight; (in order of addition) E-2350 resin 267; neutralizer, as shown; surfactant, as shown; Defo 1020 defoamer 4.00 Ultra Inc.; coalescent^a, as shown; calcium lithol pigment 50% presscake, 400-Sun Chemical Corp.; Michemlube wax 5-Michelman Inc., water, as required in order to produce a viscosity of 27 seconds using a #2 Zahn cup. Relative dry ink color intensities were measured by integrating thin film reflectance spectra at 300-600 um wavelengths using a spectrophotometer after 48 hours of drying at the above conditions

Table No. 5

| <u>Formulation</u> | <u>1</u> | <u>2</u> | <u>3</u> |
|--------------------|------------------------------|------------------------------|---------------------|
| neutralizer | 28% ammonia aq, 2.00 | 1D/2.00 | IH/1.40 |
| surfactant | Tamol 850/4.95 | 5A/1.80 | 5E/1.75 |
| coalescent | isopropanol/48 Texanol/24 | 2A/10.5 3C/15.5 4H/5.5 | 2E/20.0 |
| <u>Formulation</u> | <u>4</u> | <u>5</u> | <u>6</u> |
| neutralizer | 1F/2.00 | 1D/1.46 | 28% ammonia aq/2.00 |
| surfactant | 5K/1.55 | 5H/1.50 | Tamol 850/ 4.95 |
| coalescent | 3C/25.0 | 3C/18.0 4H/7.0 | 3C/18.0 4H/7.0 |

| | <u>Formulation</u> | <u>VOC g/l⁵</u> | <u>Dry to touch time</u> <u>hr.</u> | <u>6 hr. Heat seal</u> <u>resistance °C</u> | <u>Relative color</u> <u>intensity.</u> |
|----|--------------------|----------------------------|--|--|--|
| 5 | 1 | 144 | 3.4 | 86 | 1.00 |
| 6 | 2 | 4 | 0.7 | 154 | 1.42 |
| 7 | 3 | 3 | 0.6 | 172 | 1.27 |
| 8 | 4 | 5 | 0.7 | 104 | 1.08 |
| 9 | 5 | 4 | 0.6 | 167 | 1.39 |
| 10 | 6 | 7 | 0.6 | 122 | 1.03 |

Notes: The efficacy of the coalescent systems of the instant art in producing a faster drying, more strongly colored, and lower VOC acrylic latex based printing ink coating as compared to a conventionally coalesced counterpart are obvious from the preceding data, as are indications that incomplete application of the teachings of this disclosure may lead to inferior results. Note the deficiencies in the heat seal performance of formulation E-4 as compared to E-2, E-3, and E-5, the benefits of hyperdispersant use as indicated E-2 to E-5 vs. E-6.

Example #6

This example teaches the utility of the instant invention in the production of superior waterborne anti-scuff overprint coatings for graphic arts applications. A 30% solution of water reducible styrene-acrylic copolymer resin in water was prepared by admixture of the indicated neutralizing agent-as shown, water, and Air Product Corp's Flexbond 28 resin. Thirty parts by weight (PBW) of the preceding solution, were admixed with 50 PBW of styrene- acrylic latex resin (Flexbond 285, Air Products Corp.), coalescent, and surfactant(s) -as shown, poly ethylene wax, 2 PBW, and sufficient water to dilute the system to 100 PBW.

Measurements of VOC (by EPA Method 24), offset, and blocking limited maximum allowable impression rates (impressions/ minute [IPM]), were made. The results are given in Table 6.

| | | | |
|--------------------|-------------------|----------------------------|--------------|
| <u>Formulation</u> | <u>1</u> | <u>2</u> | <u>3</u> |
| neutralizer | 28% ammonia/ 6.00 | AMP 95 ¹ / 8.00 | AMP 95/ 8.00 |
| coalescent (s) | isopropanol/ 12 | isopropanol/ 12 | 2G/ 4.50 |
| surfactant | Tamol 850/ 2.05 | Tamol 850/ 2.05 | 5K/ 0.75 |
| <u>Formulation</u> | <u>4</u> | <u>5</u> | <u>6</u> |
| neutralizer | 1G/ 6.00 | 1G/ 6.00 | 1G/ 6.00 |
| coalescent (s) | 2G/ 4.50 | 2G/ 4.50 | 3C/ 3.65 |
| | | | 4C/ 0.85 |
| surfactant | Tamol 850/ 2.05 | 5K/ 0.75 | 2K/ 0.75 |
| <u>Performance</u> | <u>1</u> | <u>2</u> | <u>3</u> |
| VOC -g/l. | 131 | 146 | 27 |
| max IPM (offset) | 8,240 | 9,235 | 12,720 |
| max IPM (block) | 10,150 | 9,950 | 14,610 |
| <u>Performance</u> | <u>4</u> | <u>5</u> | <u>6</u> |
| VOC -g/l. | 3 | 4 | 4 |
| max IPM (offset) | 16,670 | 18,000 ² | 18,000 |
| max IPM (block) | 17,130 | 18,000 | 18,000 |